



PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to Methods of Alcoholysis of Low Grade Fatty Materials.

We, LEVER BROTHERS & UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to methods of alcoholysis of low grade fatty materials in order to obtain high grade light coloured materials therefrom. More particularly, it relates to a method for preparing very light coloured material from dark coloured fatty oils, fats and greases.

There are commercially available large amounts of very low grade fatty stocks, such as renderer's tallow and grease, which contain large proportions of free fatty acids. These materials are dark brown or black, and the dark colour is generally associated with a high free fatty acid content. These materials are quite unsatisfactory for the production of white or light coloured soaps even when purified by methods heretofore proposed. Furthermore, such purification methods are generally uneconomical when applied to such very low grade materials.

It has been proposed heretofore to hydrolyse the low grade fatty materials with water, with or without the aid of catalysts, such as the Twitchell reagents, fat-splitting enzymes or lipases, and then to distil the fatty acids liberated. Such methods are subject to many drawbacks. Hydrolysis usually results in only about 90 to 95% splitting. With low grade materials, as much as 10% may remain in the still residue as a pitch which has little value other than for use as an asphalt. Furthermore, when using low grade fatty stocks, it is generally necessary to redistil the acids and even the redistilled product is not very stable in colour. Therefore, it must be used promptly as it cannot be stored.

Another serious drawback of the foregoing type of process is that it requires equipment constructed of fatty acid resistant alloys,

since the presence of even a small amount of the ordinary structural metals quickly produces an intense coloration in the product, and also accelerates the development of rancidity.

It has also been proposed heretofore to alkali refine relatively high grade fatty stocks to remove the free fatty acids therefrom along with colouring matter and mucilaginous materials. Following this refining, the material is treated with bleaching agents such as absorptive earths or activated carbons in order to remove residual colouring matter. This process is subject to many drawbacks when applied to the low grade stocks having a high free fatty acid content. In addition to the fact that high loss is incurred as "foots" during alkali refining, a large amount of bleaching earth is required if an improved colour is to be obtained.

Other methods which have been proposed heretofore for removing colour from crude fatty materials are not commercially applicable to the low grade materials when a light coloured product of high stability is required. Such methods include oxidation with air or dichromate solutions, or reduction with sodium hydrosulphite or other reducing agents.

It is an object of the invention to provide a method for treating low grade fatty stocks having a high fatty acid content to recover therefrom high grade light coloured and colour-stable products suitable for many uses, including the manufacture of white or light coloured soap products by converting substantially all of the fatty acid components of such stock, that is, free and combined acids, into lower alkyl esters.

It has been proposed heretofore to treat higher grade fatty materials (having a relatively low free fatty acid content) with an excess of a lower alkyl alcohol in the presence of alkaline catalysts to form the lower alkyl esters of the fatty acid components of the stock which are in chemical combination as glycerides. In such pro-

cesses if the starting material contains over about 3% of free fatty acids the separation of the ester from the reaction mass is very difficult; the free fatty acids do not form esters under these conditions; rather they form soap, and the mass tends to gel and does not readily separate into layers, and so acidification is required to recover the ester. Such processes are not economical or feasible when applied to low grade fatty materials. Therefore, it is common to use refined fatty materials in such alkaline catalyst alcoholysis processes. As has heretofore been discussed, the prior refining of low grade materials results in very high losses.

It has also been proposed heretofore to treat fatty materials with a large excess of lower alcohol in the presence of an acid catalyst to prepare the lower alkyl ester of the free fatty acids initially in the stock and any developed by hydrolysis during the treatment. Such processes result in very low overall yields and are difficult to operate. In an experimental test, 100 grams of dry crude fatty material containing about 16% free fatty acids, 100 grams of methanol and 2 grams of concentrated sulphuric acid were mixed and heated with refluxing for 36 hours. Upon allowing the mass to settle, two layers formed. The ester component was present in appreciable amounts in both the upper and lower layers. A total yield of only about 30% of the theoretical amount of ester was obtained upon working up all of the reaction mass by washing, drying and distilling. Only about 14% could have resulted from alcoholysis of glycerides.

It has now been discovered that fatty stock of even the very lowest available grades may be treated by processes which are free of many of the foregoing disadvantages, and by means of which substantially all of the components of such materials may be recovered in a manner that is technically feasible and simple to operate, and also highly economical.

According to the present invention a method of alcoholysis of low grade fatty stocks containing at least 3.0% by weight of free fatty acids comprises reacting the said stocks with a stoichiometric excess of a lower alcohol under acidic conditions in the presence of an acid alcoholysis catalyst to reduce the free fatty acid content of said stocks below 3% by weight, continuing the alcoholysis reaction under alkaline conditions in the presence of an alkaline alcoholysis catalyst, stratifying the reaction mixture and separating a layer containing crude lower alkyl ester components, and distilling the crude lower alkyl esters.

Thus in this method the low grade fatty stock is reacted with a stoichiometric excess of a lower alkyl alcohol in the presence of an acid alcoholysis catalyst until the free fatty

acid content has been reduced to below 3% and preferably to about 1% or less with the result that when the reaction mixture is made alkaline, the soaps formed will not prevent separation of layers. The acid catalyst and any free fatty acids remaining may then be neutralised by adding an alkaline material, and an additional amount of alkaline material to act as alcoholysis catalyst added. In the presence of the alkaline catalyst, the alcohol reacts rapidly with the glyceride esters to form the lower alkyl ester of the fatty acids in the glyceride, and also glycerine as a by-product. After a short period of standing the material readily stratifies or separates into two layers, the upper of which contains substantially all of the crude alkyl esters of the fatty acid, most of the unreacted fatty material, some excess alcohol, and a small amount of soap; and the lower of which contains the glycerine, a negligible amount of unreacted fatty material, practically all of the unreacted lower alkyl alcohol, a negligible amount of the ester, soap and salts of the acid catalyst used. For practical purposes, the upper layer contains the ester and the lower layer contains the glycerine and unreacted alcohol. The crude ester layer is separated, and may be washed with a small amount of water to remove any glycerine and soap, and then subjected to distillation at reduced pressures. A high grade light coloured and colour-stable lower alkyl ester product of fatty acids is obtained as distillate in very high yields. The still residue contains most of the unsaponifiables and other impurities of the fatty stock.

An important factor contributing to the success of the invention is the discovery that very high conversion of the fatty acids to the lower alkyl esters may be obtained, even in the presence of so-called impurities, by the sequence catalysis employed, to wit, acid catalysis then alkaline catalysis of the whole reaction mass without intermediate removal of esters. This sequence catalysis distinguishes the invention over heretofore proposed processes.

In a preferred embodiment of the invention, the lower layer is acidified. Upon acidification, an upper dark fatty layer usually separates; slight dilution with water aids this. It contains most of the coloured impurities of the starting materials not carried into the ester layer. This layer is separated from the lower glycerine-water layer and added to the next batch of starting materials.

Alternatively, the lower layer may be acidified and heated to refluxing to convert the fatty acids of the soaps to the lower alkyl esters of the alcohols present. If necessary for this, additional alcohol may be added also. Then the crude ester product

may be separated and its ester recovered as above.

The glycerine may be recovered from the acidified lower layer in concentrated form.

5 It contains only small amounts of salts of the alkaline catalyst and free acid as impurities and may be purified by neutralisation and distillation at reduced pressures. However, if only small amounts of water have
10 been added during the treatment, the glycerine may be utilised without purification for some purposes, such as for example, in the manufacture of glyptal resins. The wash liquors may be worked up to recover the
15 glycerine in the usual manner, and purified and concentrated by distillation at reduced pressures. The wash liquors and the lower layer may be combined and then worked up to recover glycerine as above in one opera-
20 tion.

The excess alcohol may be recovered from the ester layers and the glycerine layers in the usual solvent recovery processes, and re-used.

25 If the lower alkyl ester is used in making soap, the alcohol evolved thereby may also be recovered in a solvent recovery system and may be re-used in the processes.

30 In the apparatus for the distillation of the esters, the usual structural materials may be used, so that the high cost of special resistant alloys is avoided. This results in a great saving in cost.

35 The ester distillation residues may be treated to recover any small amount of saponifiable material therein, and also to recover unsaponifiable material; the latter has a high sterol content and may be used as a lanolin substitute. Thus, in accordance
40 with the invention, even impurities in the fatty materials may be recovered as valuable by-products.

45 The process is applied to the type of fatty stock containing at least 5.0% by weight of free fatty acid, and preferably at least 10.0% by weight thereof.

50 From just over 1.0 equivalents to about 10.0 equivalents lower alkyl alcohol may be used per equivalent of total fatty acid (free and combined) in the fatty stock, and preferably from about 2.0 to about 4.0 By "lower" alcohols, those which contain one, two, or three carbon atoms are intended: of these methanol is preferred.

55 As acid alcoholysis catalysts for the first step in the process, a wide variety of commercial materials may be used, such as sulphuric, phosphoric, hydrochloric, sulphonic acids such as toluene sulphonic acid and camphor sulphonic acids, metallic salts, etc.; commercial 66° Baumé sulphuric acid is economical and readily available and is
60 therefore used for illustrative purposes. The concentration of the catalyst used is equivalent to about 0.3 to 1.0% of sulphuric acid

based on the weight of the fatty stock.

Any convenient alkaline material may be used for the neutralisation provided it does not introduce substantial amounts of water into the reaction mass. An alkali metal
70 alcoholate or a caustic alkali is suitable. The preferred alkaline alcoholysis catalyst is an alkali metal compound and is usually present in a concentration of from about 0.1 to about 1.0% of the weight of the fatty
75 stock, calculated as the hydroxide. The alcoholate may be prepared *in situ* or separately from alkali metal and alcohol. The hydrogen evolved thereby could be used to hydrogenate and thereby greatly improve
80 the stability of the esters.

The ester may be distilled at 3 mm. Hg absolute pressure at from about 125° to 200° C., and preferably from 150° to 200° C.

85 The following examples will serve to illustrate the invention. The various steps described are also diagrammatically shown in the accompanying drawings in which Figures 1, 2 and 3 are flow sheets for Examples 1, 2 and 3 respectively.
90

EXAMPLE 1

1375 parts by weight of dry, dark brown, fatty grease containing 20.3% free fatty acid (as oleic), 540 parts by weight of commercial methanol and 10 parts by weight of
95 66° Baumé commercial sulphuric acid were mixed and heated to refluxing with agitation for 3 hours; then agitation was stopped and the mixture cooled slightly so that refluxing
100 ceased. An upper layer of methanol containing a small amount of methyl esters formed upon standing. Without otherwise disturbing or altering the contents of the reaction mixture, 10 parts by weight of
105 metallic sodium was then added in small increments. It floated upon the upper layer and reacted with the methanol therein to form sodium methylate. When this reaction ceased, the two layers were intimately mixed. Then the reaction mixture was allowed to
110 stand for 15 minutes at slightly below the boiling point of methanol. Two layers again formed. The upper ester layer was separated and washed twice with 140 parts
115 of water each time, at 70 to 75° C. The wash liquors were added to the bottom layer.

In a commercial process the lower layer would preferably be acidified with concentrated acid, refluxed until the free fatty acids liberated from the soap were esterified,
120 and the ester product formed as a result thereof would be separated and added to the above described upper ester layer or accumulated and subsequently distilled.

125 Similar steps were carried out in this run. The lower layer was acidulated with sulphuric acid and heated. The fatty acids which separated were converted to methyl esters by refluxing with 200 parts of methanol

and 3.0 parts of sulphuric acid, calculated as concentrated acid and diluting with water. The esters which formed and which amounted to about 10% of the original material were separated and combined with the main ester layer.

The combined crude methyl ester mass was distilled at 3 mm. Hg absolute pressure and from 150 to 200° C. A substantially water white ester was obtained, which amounted to 95% of theoretical yield based on the fatty acid content of the stock. The still residue that remained was about 5% of the starting stock material.

The lower layer consisted of a glycerol in water solution which contained only a small amount of sodium sulphate and dilute sulphuric acid as impurities.

EXAMPLE 2

1375 parts by weight of crude dry house (kitchen scrap) grease containing 18.9% free fatty acid (as oleic) and 1.30% unsaponifiable matter, 490 parts by weight of commercial methanol and 10 parts by weight of 66° Baumé commercial sulphuric acid were mixed and heated to refluxing with agitation for 2 hours. 22 parts by weight of anhydrous potassium carbonate was slowly added and refluxing was continued for 1 hour. Then the mass was allowed to settle for 30 minutes at somewhat below the boiling temperature of methanol. It formed two layers. These layers were separated.

In a preferred embodiment of the invention, in practice, the upper layer would be distilled to recover methyl esters therefrom. The lower layer would be acidified; the upper layer formed as a result thereof would be added to the next charge, and the lower layer resulting would be worked to recover glycerine.

In this experiment, the top layer was washed at 70° C. with 138 parts by weight of water and allowed to settle. The wash liquors were acidified with sulphuric acid and allowed to settle. An upper layer of fatty acids formed thereon; this upper layer was separated and added to the main bottom layer. The resulting mixture was acidified with a solution of 20 parts by weight of 66° Baumé commercial sulphuric acid in 20 parts by weight of commercial methanol, and heated to refluxing with agitation for two hours. An equal weight of water was added and the mixture allowed to settle. It formed into two layers. The upper layer was separated and added to the main washed top layer. This mixture of crude esters was washed at 70° C. with 138 parts by weight of water, allowed to settle, and vacuum dried. 1383 parts by weight of crude methyl esters containing 0.40% free fatty acids and 1.49% unsaponifiable matter was obtained.

The crude methyl esters were distilled at

3 mm. Hg absolute pressure from 150 to 190° C. 1188 parts by weight of white methyl esters containing 0.25% free fatty acids and 0.57% unsaponifiable matter was obtained. This is 86.6% of the total fatty components of the original fatty material. 195 parts of still residue was obtained. It was saponified, acidified, re-esterified, diluted, allowed to settle and distilled as above. 150 parts by weight of the white methyl ester was obtained thereby. This is 11.0% of the total fatty components of the original fatty material. The 45 parts by weight of still residue remaining (from the second distillation) was saponified, extracted with ether, and the extract recovered from the ether. 12 parts by weight of unsaponifiable matter or sterol of good colour and 30 parts of fatty acid soapstock were obtained.

In a preferred commercial embodiment of the invention, the fatty acid layer separated from the saponified and then acidified still residue would be added to an initial esterification charge, and the residue remaining could then be extracted to recover sterols.

The wash liquors and main bottom layer were combined and heated until the methanol and some water were driven off. Crude glycerol of about 33% strength was recovered. It amounted to 106 parts by weight as 100% glycerine, that is 96% of the glycerine content of the original material.

EXAMPLE 3

331 parts by weight of crude dry house (kitchen scrap) grease containing 16.41% free fatty acid and 95.1% total fatty matter, 133 parts by weight of commercial methanol and 3.3 parts by weight of 66° Baumé commercial sulphuric acid were mixed and heated to refluxing with agitation for 90 minutes. Heating and agitation were stopped and the mass allowed to settle for about 5 minutes at somewhat below the boiling point of methanol. Two layers formed. 2.4 parts by weight of metallic sodium was carefully added. It reacted with the methanol in the upper layer to form sodium methylate in situ. After about 15 minutes this reaction was completed; the mass was then thoroughly mixed and allowed to stand for 30 minutes at somewhat below the boiling point of methanol. It formed into two layers. The bottom layer was withdrawn and the top layer was given 3 consecutive water washes at 70° C., each of 30 parts by weight of water. Then the top layer was distilled at 3 mm. Hg absolute pressure and at from 160 to 200° C. 290 parts by weight of white methyl esters was obtained as distillate. 11 parts by weight of still residue was obtained.

In a preferred commercial embodiment of the invention, this still residue would be treated as indicated in Example 2.

In the present case, this still residue, the wash liquors and main bottom layer were mixed, 8 parts by weight of sodium hydroxide was added and the mixture heated to about 83° C. The greater part of the methanol present was driven off. The mixture was acidified with 10 parts by weight of 66° Baumé commercial sulphuric acid. The fatty matter which formed into an upper layer was removed, mixed with 90 parts by weight of commercial methanol and 1.8 parts by weight of 77° Baumé commercial sulphuric acid and heated to refluxing with agitation for 90 minutes. The reaction mass was diluted, allowed to settle, and washed with water, dried and distilled as above. 31 parts by weight of white methyl esters were obtained as distillate. 10 parts by weight of still residue were obtained. 2.5 parts by weight of sterols of good colour were recovered from this residue by saponification and ether extraction. 7 parts by weight of 80% fatty acid material were also recovered therefrom as extracted residue.

In all, 321 parts by weight of water-white esters of 95.51% total fatty matter was obtained. This is 97.4% of the total fatty matter of the original fatty material. 2.5 parts by weight of sterol of good colour were also obtained.

In the present invention, coupled with the marked advantages that the new process presents in its use of raw materials, the equipment required is simpler and less critical than that of heretofore proposed distillation purification processes.

In commercial operation the alkaline liquor comprising the lower layer in the process according to the invention instead of being treated to extract the esters therefrom as in the examples given above, could be used to neutralise the reaction mass in a subsequent acid alcoholysis in either a batch or continuous manner. The alkaline soaps in the alkaline liquor would then react with the acid catalyst to release the fatty acids which would then be esterified by the lower alcohol. These last two reactions would proceed simultaneously with the alkaline alcoholysis of the fatty stock according to the process of the invention.

This procedure would result in a saving of material and in the elimination of the extra and independent step of recovering fatty acids from the alkaline soaps by acidification as in the examples given above. Furthermore, only one separation of all the esterified material would be necessary.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of alcoholysis of low grade fatty stocks containing at least 5.0% by weight of free fatty acids which comprises reacting the said stocks with a stoichiometric excess of a lower alcohol under acidic conditions in the presence of an acid alcoholysis catalyst to reduce the free fatty acid content of said stocks below 3% by weight, continuing the alcoholysis reaction under alkaline conditions in the presence of an alkaline alcoholysis catalyst, stratifying the reaction mixture and separating a layer containing crude lower alkyl ester components, and distilling the crude lower alkyl esters.

2. A method according to claim 1 wherein said lower alcohol is methanol.

3. A method according to claim 1 or 2 wherein said acid catalyst is sulphuric acid.

4. A method according to any of the preceding claims wherein said treatment with lower alcohol and acid catalyst is carried out under refluxing.

5. A method according to any of the preceding claims wherein said alkaline catalyst is potassium carbonate.

6. An improved method of alcoholysis of low grade fatty stocks substantially as herein described.

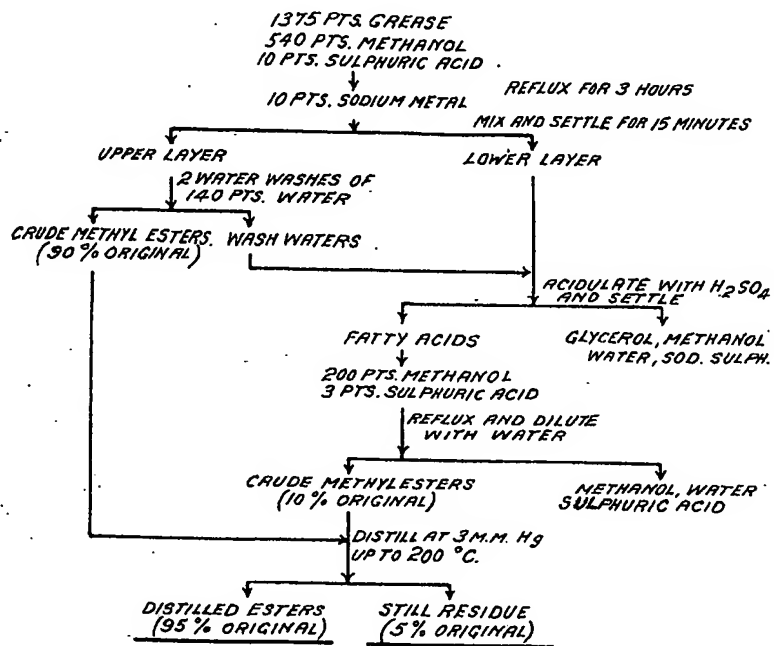
7. Lower alcohol esters of fatty acids when prepared from low grade fatty stocks by the method claimed in any of the preceding claims.

Dated this 29th day of May, 1946.

LEVER BROTHERS & UNILEVER
LIMITED.

R. JONAS,

Acting for the Applicants.

Fig. 1.

[This Drawing is a reproduction of the Original on a reduced scale.]

Fig. 2.

[This Drawing is a reproduction of the Original on a reduced scale.]

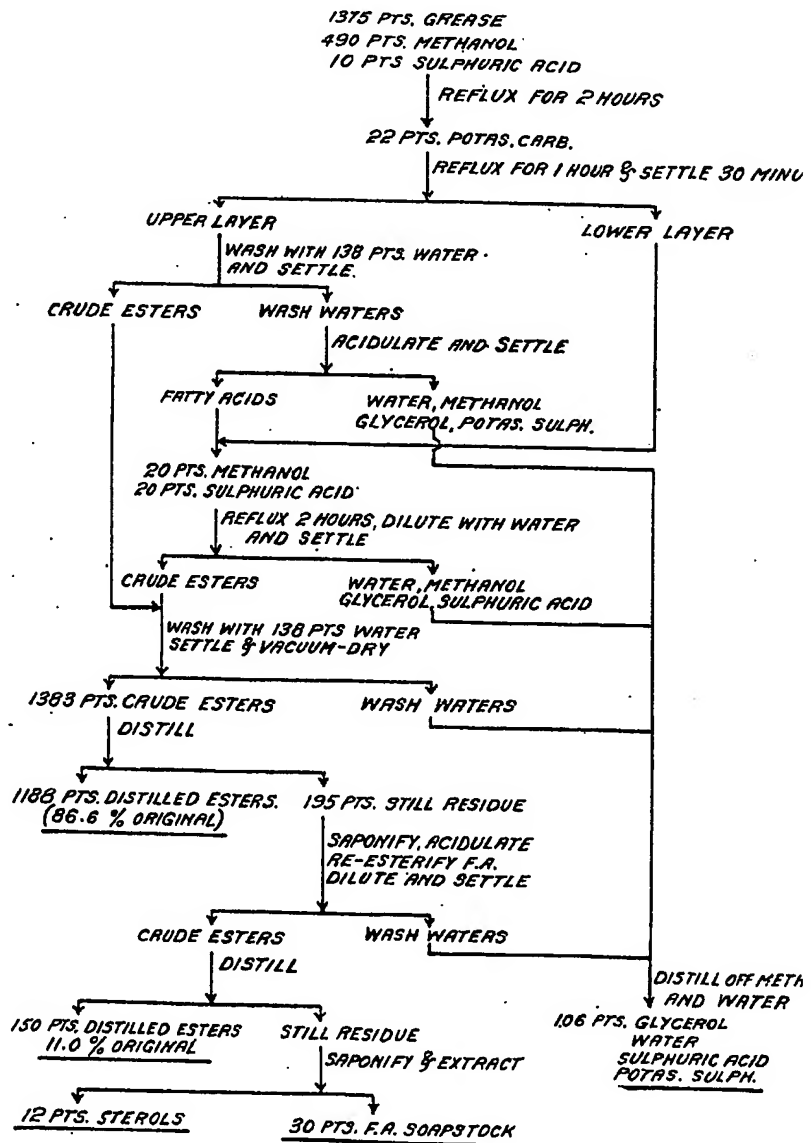


Fig. 3.

30 MINUTES

ER

1.1 OFF METHANOL
WATER
OL
16 ACID
ULPH.

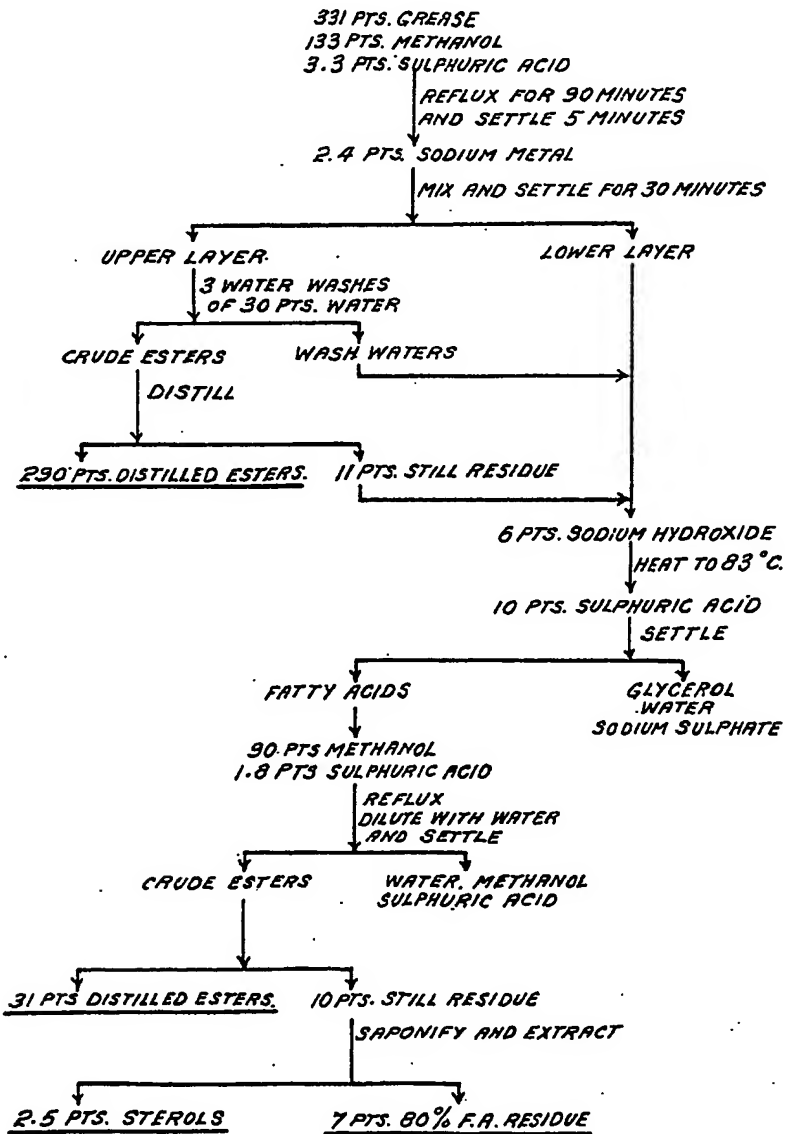


Fig. 3.

